

## NEGATIVE-ION MASS SPECTRA OBTAINED WITH THE AID OF AN ELECTRON-IMPACT SOURCE

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*The negative-ion mass spectra of six natural compounds of various classes, obtained with the use of an EI ion source, have been characterized. The conditions for obtaining the spectra presuppose the occurrence of a process of secondary-electron capture.*

In connection with the introduction of a system for recording secondary negative ions [LSIMS<sup>(-)</sup>] on a MKh 1310 mass spectrometer by us together with a worker from the Spektron OKB [Experimental Design Bureau] (St. Petersburg), the possibility has also been established of obtaining informative negative-ion (NI) mass spectra with the aid of an IÉ-24 ion source. Since in the recording of the EI NI spectra all the conditions necessary for obtaining positive-ion spectra (direct introduction of the sample with preheating of the bulb and the ionization chamber to 250°C, ionizing voltage  $\approx 70$  V, collector current  $\approx 100 \mu\text{A}$ ) were reproduced, the resulting NI mass spectra should most probably have been formed as the result of a process of secondary-electron capture (SEC) [1, 2]. However, a series of recurring characteristics of all the spectra and, above all, the predominant formation of the  $(M - H)^-$  ions and, in individual cases, the recording of cluster ions showed that, in addition to SEC, ion-molecule reactions and the formation of ion pairs could take place in the EI ion source. The realization of the first of these processes was possible because in the IÉ-24 source the flow of primary electrons proceeds through a zone of increased pressure of the vapors of the sample at the outlet from the evaporator bulk (conditions close to the "in beam" regime are created). The SEC variant of MS under consideration deserves urgent attention, in part, as an alternative to the CI NI method that has been most widely represented in the literature of the last decade.

As an example, we shall give details of the EI NI mass spectra of six compounds of natural origin: a sesquiterpene of the carotane series, ferutinin (I) [3]; the chlorine-containing guaiane lactone hyrcanin (II) [4]; the steroid sapogenin diosgenin (III); ecdysterone (IV); an aglycon of cardenolide nature, strophanthidin (V); and the sterol glycoside alloside B (VI) [5]. The formulas of these compounds are given below, the dotted lines showing the modes of formation of the fragmentary ions. The mass numbers and relative intensities of the peaks are given in Table 1.

In the EI positive-ion (PI) mass spectra of the compounds under consideration, apart from diosgenin, the  $M^+$  ions are unstable. On the other hand, the peaks of the  $(M - H)^-$  ions are some of the strongest in the EI NI spectra of (I), (II), (III), and (V). This fact indicates that in many cases thermolability is not the decisive factor for the absence of the  $M^+$  peaks in the EI PI spectra.

Let us now consider the pathways of the fragmentation of the NIs in the spectra of (I)-(VI) and those features which distinguish them from the PI spectra of the corresponding compounds.

On the breakdown of ferutinin (I) it is predominantly the bonds of the *p*-hydroxybenzoic acid residue that are cleaved, the peak of ions with  $m/z$  137 being the maximum while the peak of ions from the sesquiterpene nucleus with  $m/z$  219 have a substantially lower intensity. The ejection of the isopropyl radical from C-4, resulting in the instability of the molecular ion, that is characteristic for the PI spectra does not take place in the EI spectra.

By analogy with ferutinin, in the EI NI spectrum of hyrcanin the peak of the ions of the 3-chloro-2-hydroxybutyric acid residue with  $m/z$  137/139 has the maximum intensity, the contribution of the charged product of the splitting out of this acid ( $m/z$  296) being small. In the region of high mass numbers in this spectrum the successive elimination of two molecules of HCl and a molecule of water is observed. No breakdown of the guaiane skeleton is detected in the spectra of (I) and (II),

TABLE 1. Mass Numbers and Relative Intensities of the Peaks of Ions in the EI NI Spectra of Compounds (I)-(VI)

Compound	<i>m/z</i> ( <i>I</i> , %)
I	357(44), 330(5), 280(8), 219(19), 167(13), 137(100), 136(25), 121(28), 94(35), 93(43)
II	433/435/437(12/9/2), 398/400(5/2), 380/382(2/1), 362(6), 344(3), 296/298(5/2), 137/139(100/33)
III	413(100), 395(9), 343(9), 143(8), 113(38)
IV	479(5), 462(100), 460(33), 444(8), 426(3), 374(1), 344(8), 329(4), 302(9), 287(3), 272(3), 159(5), 115(1), 85(2)
V	403(100), 385(48), 367(12), 359(45), 357(47), 355(31), 341(15), 329(11), 313(17), 303(16), 179(6), 178(5), 125(9), 123(6), 111(3), 109(3), 97(10), 81(7)
VI	757(0,5), 739(0,4), 723(0,6), 667(0,5), 654(0,4), 637(0,7), 623(0,3), 595(72), 577(75), 433(10), 415(7), 413(9), 251(2), 249(1), 235(1), 179(8), 161(17), 143(12), 125(10), 119(13), 113(18), 101(33), 97(17), 96(24), 89(13), 71(100)

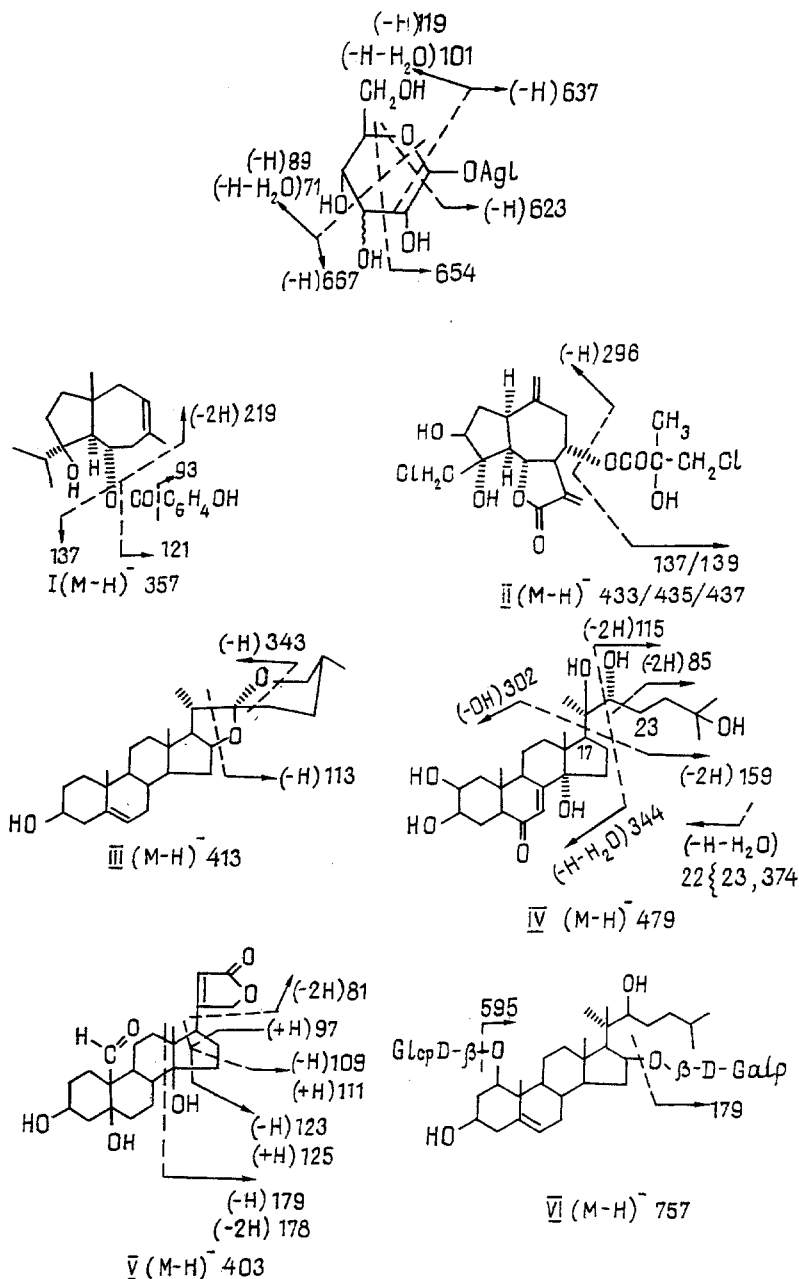
in contrast to the EI PI spectrum of hyrcanin [6]. The EI NI spectrum of (II) practically coincides with the CI NI (methane) spectrum of this compound, which apparently confirms the occurrence of ion-molecule reactions in the IÉ-24 source.

The polycyclic system of the diosgenin (III) molecule and the presence of a single polar substituting group makes it resistant to breakdown on dissociative electron capture. There is only a selective rupture of the bonds adjacent to the spiroketal grouping, which leads to ions with *m/z* 343 and 113.

Ecdysterone (IV) behaves in a nonstandard fashion. The low intensity of the peak of the (M — H)<sup>–</sup> ion is associated here with the 100% height of the peak of the (M — H<sub>2</sub>O)<sup>–</sup> ions (*m/z* 462). The most probable structures of these ions can be judged only after the study of the EI NI mass spectra of a number of ecdysteroids. So far as concerns the breakdown of the carbon chain of ecdysterone, it takes place at the same bonds as in the EI PI mass spectra. This is, possibly, evidence in favor of the formation of ion pairs. However, the general pattern of the NI spectrum differs sharply from the PI spectrum. Thus, as the result of the cleavage of the C-20—C-22 bond, among the series of ions with *m/z* 363, 345, 327, 309 [7, 8] the peaks of ions with *m/z* 344 and 329 appear; in place of the triplet of ions with *m/z* 301, 300, and 299 (cleavage of the C-17—C-20 bond) there are peaks of ions with *m/z* 302 and 287. The breakage of the same bonds and localization of the charge on the side chain forms ions with *m/z* 115 and 159. In contrast to the PI spectra, they are stabilized without the loss of a molecule of water. Indications of breakdown at the C-22—C-23 bond — ions with *m/z* 374 and 85 — are observed in the NI spectrum. Analogues of the latter are totally uncharacteristic for the PI spectrum of ecdysterone.

The EI NI spectrum of strophanthidin (V) has sufficient informativeness for this method to be used in structural investigations of similar compounds. Together with the 100% peak of the (M — H)<sup>–</sup> ions having *m/z* 403, the peaks of the products of breakdown at the bonds of rings *C* and *D* are clearly shown in it. The localization of the charge takes place on elements of the structure including the lactone ring, while in the EI PI spectrum the charge is localized predominantly on the atoms of rings *A—C* [9, 10]. The greatest contribution to the total ion current in the NI spectrum of (V), as in the PI spectrum, is made by processes involving the splitting out of the oxygen substituents in the form of H<sub>2</sub>O and CO. In addition, the splitting out of CO<sub>2</sub> from the lactone ring takes place here.

The presence of the peak of (M — H)<sup>–</sup> ions in the spectrum of the bioside (VI) shows most clearly that the absence of the M<sup>+</sup> peak from the EI PI spectrum of the same compound [11] is due not to thermolability but to the instability of this ion to EI. In the NI spectrum of (VI) three types of fragmentary ions are observed: a) the products of the successive elimination of the pyranose units (*m/z* 595 and 433); b) anions of the sugar residues with *m/z* 179, and the products of their degradation with *m/z* 161, 143, and 125; and c) the products of the breakage of the bonds of the pyranose rings, formed by the scheme given below.



Ions of type *c* with high mass numbers ( $m/z$  667, 654, 637, 623) are characteristic to some degree or other of the PI spectra of glycosides [12]. On the other hand, ions of types *b* and *c*, which are present in the low-mass region of the NI spectrum of alloside B (VI) are uncharacteristic for PI spectra and may therefore be useful in structural investigations of glycosides. In the central part of the spectrum of VI there are the peaks of ions with  $m/z$  251, 249, and 235, which are characteristic for the spectrum of the corresponding aglycon and therefore most probably include the C<sub>18</sub> substituent of the steroid skeleton.

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